Table III. Interatomic Distances (Å)

	dist	cor[a]
U-3N	2.237 (9)	2.240
N-2Si	1.727 (5)	1.740
Si-C(1)	1.86 (1)	1.89
Si-C(2)	1.86 (1)	1.90
Si-C(3)	1.84 (1)	1.88

[a] Adjusted for thermal motion with the assumption of the "riding model".

Table IV. Selected Angles (Deg)

N-U-N	115.0 (1)	N-Si-C(2)	113.3 (5)
U-N-Si	127.1 (3)	N-Si-C(3)	106.8 (5)
U-N-Si[a]	106.9 (2)	C(1)-Si-C(2)	107.9 (6)
Si-N-Si[a]	125.3 (6)	C(1)-Si-C(3)	107.8 (6)
N-Si-C(1)	112.5 (4)	C(2)-Si-C(3)	108.3 (5)

[a] Atom at position x, $x - y$, $^1/_2 - z$.

in the final difference Fourier map was ~0.8 e Å^{-3} about 1 Å from the U atom. The second and third peaks were each ~0.3 e Å^{-3} and were in the channel along the z axis; none of the residual density in the hole could be related to any chemically reasonable structure.

Weissenberg photography, using Cu Kα X-rays, was used to determine the cell dimensions of the isomorphous complexes of U(III) and Th(IV). Table I summarizes these results. Unfortunately the crystal quality of these compounds was very poor and crystal structure determinations were not attempted.

Results and Discussion

Atomic parameters, distances, and angles are listed in Tables II–IV; an ORTEP drawing of the structure is shown in Figure 1. The uranium atom is on a crystallographic 3-fold axis and bonded to three nitrogen atoms. It is disordered in the z direction at locations 0.51 Å above and below the plane at $z = {}^1/_4$. The electron density in the channel, that runs parallel to c at the origin, is attributed to pentane solvent molecules in highly disordered arrangements.

Although $[(Me_3Si)_2N]_3UH$ is isostructural with the binary silylamides of the lanthanide derivatives which have been structurally characterized (Nd,[5] Eu,[6] and Yb[7]), the uranium is tetravalent. The uranium–nitrogen bond length of 2.24 Å is very close to those previously found for terminal, tetravalent uranium–nitrogen bond lengths in $[U(NEt_2)_4]_2$, $[U(MeNCH_2CH_2NMe)_2]_3$, $[U(MeNCH_2CH_2NMe)_2]_4$, and $[U(NPh_2)_4]$ which are 2.22,[11] 2.21,[12] 2.27,[13] and 2.24 Å,[14] respectively. The thorium(IV)–nitrogen bond length in the six-coordinate tetrahydroborate derivative $Th[N(SiMe_3)_2]_3BH_4$ is 2.32 Å.[15] The ionic radius of thorium(IV) is estimated to be ca. 0.05 Å larger than that of uranium(IV).[16] Hence, a uranium(IV)–nitrogen bond length of ca. 2.27 Å can be estimated, in good agreement with the observed value. Since the ionic radius of uranium(III) is ca. 0.08 Å longer than that of thorium(IV), a uranium(III)–nitrogen bond length can be estimated to be ca. 2.4 Å, much longer than that observed. Thus, the U–N bond length in $[(Me_3Si)_2N]_3UH$ supports the identification as a compound of tetravalent uranium.

Unfortunately, a suitable crystal for a structure determination of the uranium(III) silylamide $U[N(SiMe_3)_2]_3$ could not be obtained, but it was found to be isostructural with that of the hydride $HU[N(SiMe_3)_2]_3$. However, the larger cell dimensions and volume (Table I) of the trivalent species are consistent with the fact that uranium(III) is larger than uranium(IV). Further, the similarity of the cell dimensions and volume of the isostructural thorium hydride $[(Me_3Si)_2N]_3ThH$ with those of $[(Me_3Si)_2N]_3U$ indicates that uranium(III) is similar in size to thorium(IV).

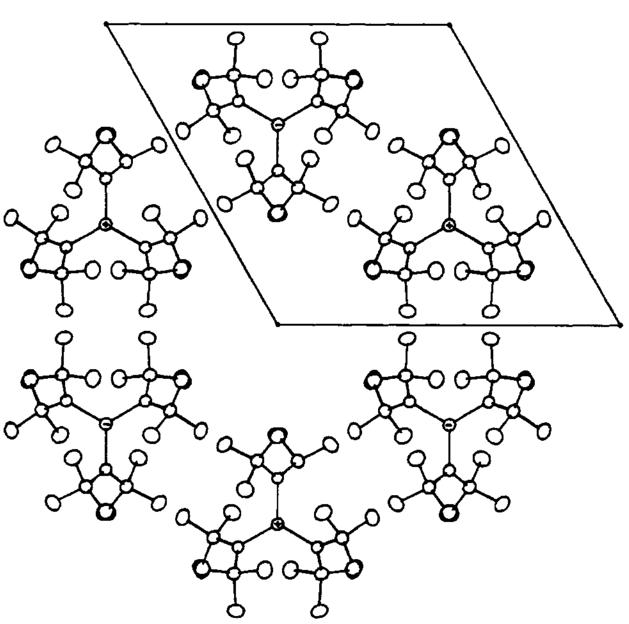

Figure 1. Packing diagram as seen down the c axis.

The hydride ion position could not be located, which is not surprising considering the usual difficulty in finding hydrogen atoms in structures containing very heavy atoms, especially in this case where the considerable disorder degrades the resolving power of the diffraction data.

Acknowledgment. This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract No. W-7405-ENG-48.

Registry No. $[(Me_3Si)_2N]_3UH$, 70605-08-2; $[(Me_3Si)_2N]_3ThH$, 70605-07-1; $U[N(SiMe_3)_2]_3$, 69927-52-2.

Supplementary Material Available: Data processing formulas and the listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Inorganic and Analytical
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Jerusalem, Israel

Species with a Triple Molybdenum to Molybdenum Bond in Aqueous Solution

Avi Bino

Received January 16, 1980

The existence of species containing multiple molybdenum to molybdenum bonds in aqueous solutions was reported by several investigators. Bowen and Taube[1] investigated the product of the reaction between $Ba(TFM)_2$ and $Mo_2(SO_4)_4^{4-}$ in the noncomplexing acid solutions of trifluoromethylsulfonic acid (HTFM). They identified the resulting red ion as $[Mo\overset{4}{-}Mo]^{4+}$(aq). Pernick and Ardon[2] reported the existence of a stable dimolybdenum species in the 2.5+ oxidation state

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(1) Bowen, A.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287.

(2) Pernick, A.; Ardon, M. *J. Am. Chem. Soc.* **1975**, *97*, 1255.

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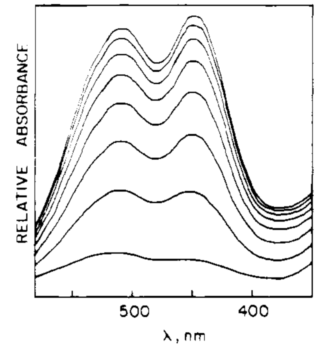

Figure 1. Spectral change in reaction 1b.

with a bond order of 3.5 in aqueous H_2SO_4. This complex, $Mo_2(SO_4)_4^{3-}$, undergoes disproportionation in aqueous HCl or *p*-toluenesulfonic acid (HPTS). One of the products of this process was identified as a molybdenum(II) species, $[\mathrm{Mo}\overset{4}{-}\mathrm{Mo}]^{4+}$(aq). The second product has not been identified.[2] The reversibility of the disproportionation reaction was demonstrated by the addition of SO_4^{2-} ions to the disproportionation mixture which regenerated $Mo_2(SO_4)_4^{3-}$ quantitatively. A blue-gray solution of a phosphato complex of the unit $[\mathrm{Mo}\overset{3.5}{-}\mathrm{Mo}]^{5+}$ has also been prepared in aqueous H_3PO_4.[3]

Compounds with molybdenum to molydenum triple bonds were prepared and characterized structurally.[4] Most of these compounds are extremely air and moisture sensitive. Recently, the preparation and structure determination of new compounds which contain the unit $Mo_2(HPO_4)_4^{2-}$, with molybdenum to molybdenum triple bonds, were reported.[5] These compounds are stable in the laboratory atmosphere.

This work reports the existence, in aqueous solution, of molybdenum(III) species derived from the unit $[\mathrm{Mo}\overset{3}{-}\mathrm{Mo}]^{6+}$. The first, having the general composition of $[Mo_2Cl_n(H_2O)_{8-n}]^{(6-n)+}$ (I) is obtained from $Mo_2(SO_4)_4^{3-}$ by the disproportionation of the $[\mathrm{Mo}\overset{3.5}{-}\mathrm{Mo}]^{5+}$ core in 1 M HCl, as well as by a two-electron oxidation of the $[\mathrm{Mo}\overset{4}{-}\mathrm{Mo}]^{4+}$ unit in the same medium. The second, $Mo_2(HPO_4)_4^{2-}$ (II), is obtained by dissolving its salts in aqueous H_3PO_4.

The HPO_4^{2-} ligands in II can be substituted by Cl^- to produce I.

Experimental Section

$K_4Mo_2Cl_8$, $(C_5NH_6)_3[Mo_2(HPO_4)_4Cl]$, and $K_3Mo_2(SO_4)_4 \cdot 3^1/_2H_2O$ were prepared as described previously.[2,5,6] Fluka Dowex 50W-X2 cation-exchange resin (100–200 mesh, H^+ form) and Dowex 1-X8 anion-exchange resin (100–200 mesh, Cl^- form) were used for the separation of the disproportionation products. All ion-exchange chromatography was conducted under nitrogen at ca. 2 °C. All UV–vis spectra were recorded at room temperature under inert atmosphere. Cary-14 and Perkin-Elmer 402 spectrophotometers were used for spectral measurements.

Results

Disproportionation of $Mo_2(SO_4)_4^{3-}$ in HCl (1 M). $K_3Mo_2(SO_4)_4 \cdot 3^1/_2H_2O$ (0.1 g) was dissolved in 50 mL of HCl (1 M) under nitrogen at room temperature. The spectral change between 350 and 650 nm was recorded till the reaction was completed (about 5 min at 25 °C). The results are shown in Figure 1. At $t = 0$, the solution contains mostly $Mo_2(SO_4)_4^{3-}$ which has almost no absorption in this region.[2] Two peaks grow as the reaction advances. One at 510 nm belongs to the molybdenum(II) species $[Mo_2]^{4+}$(aq). The second one has a maximum at 430 nm and belongs to I, vide infra.

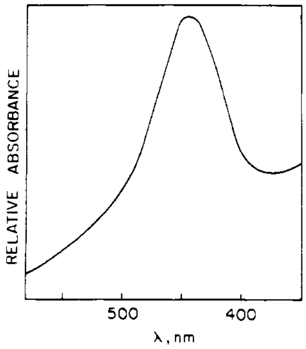

Figure 2. Absorption spectrum of I.

Table I. Oxidation State of Molybdenum in I

	mL of 0.1 N $KMnO_4$		
sample	before JR	after JR	oxidn state[a]
1	3.54	3.55	3.0+
2	2.04	2.04	3.0+
3	4.51	4.52	3.0+

[a] The average oxidation state is (3.0 ± 0.1)+.

Table II. Oxidation State of Molybdenum in the Yellow-Green 2+ Cation

	mL of 0.1 N $KMnO_4$		
sample	before JR	after JR	oxidn state[a]
1	4.60	4.75	3.1+
2	4.30	4.30	3.0+
3	6.14	6.11	3.0+

[a] The average oxidation state is (3.0 ± 0.1)+.

Table III. Cl/Mo Ratio in the Yellow-Green 2+ Cation

sample	mL of 0.1 N $KMnO_4$	mmol of Mo	mmol of Cl^-	Cl/Mo ratio[a]
1	4.75	0.158	0.325	2.06
2	4.35	0.145	0.297	2.05
3	6.01	0.200	0.390	1.95

[a] The average Cl/Mo ratio is 2.02 ± 0.06.

The disproportionation mixture was then diluted and absorbed on a Dowex 1-X8 anion-exchange column in the Cl^- form. A red band at the top of the column was observed. The band contained the unit Mo_2^{4+} as an anionic chloro complex.[7] The color of the solution that passed through the column was yellow-green, and its spectrum is shown in Figure 2. It has a single band at 430 nm. The oxidation number of species I in this solution was determined,[8] and the results of three independent experiments are given in Table I. The average

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(3) Solutions of Mo_2^{5+} in H_3PO_4 were prepared by oxidation of Mo_2^{4+} in this medium (unpublished results).

(4) For review see: Bino, A.; Cotton, F. A. *Chem. Uses Molybdenum, Proc. Conf., 3rd* **1979**, 1–8.

(5) Bino, A.; Cotton, F. A. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 332; *Inorg. Chem.* **1979**, *18*, 3562.

(6) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7.

(7) Pernick, A. Ph.D. Thesis, Hebrew University, Jerusalem, 1974, pp 27.

(8) Oxidation number determination: The oxidation number of the yellow-green ion was determined as follows. Aliquots of this ion in H_2SO_4 (0.5 M) were titrated with $KMnO_4$ to Mo(VI). The oxidized solutions were then reduced with a Jones reductor (JR) to Mo(III) and discharged into excess Fe(III). The Fe(II), resulting from oxidation of Mo to Mo(VI) was titrated with $KMnO_4$. The oxidation number is given by the ratios between the $KMnO_4$ solution volumes before and after the reduction with JR according to: oxidation number = 6 − [(mL of MnO_4^- before JR)/(mL of MnO_4^- after JR)] × 3.

(9) Cl/Mo ratio determination: Aliquots of the yellow-green ion eluted from the cation-exchanger column with 0.5 M H_2SO_4 were titrated with $KMnO_4$. An excess of $AgNO_3$ solution was added to the resulting solutions and then back-titrated with KNCS as previously described.[11] Control experiments showed that the Mo(VI) and Mn(II) ions, present in the solutions, did not interfere with the chloride determination. All titrations of the yellow-green ion with $KMnO_4$ were conducted under nitrogen at 0 °C.

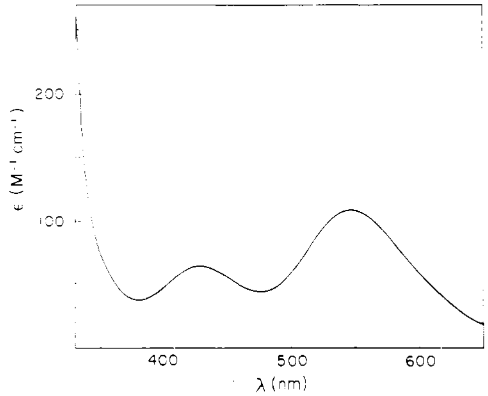

Figure 3. Absorption spectrum of $Mo_2(HPO_4)_4^{2-}$ (II) in H_3PO_4 (2 M).

oxidation number is (3.0 ± 0.1)+. The reduction of this yellow-green solution with a JR yielded a red solution of $[Mo_2]^{4+}(aq)$.[10]

The yellow-green solution was absorbed on a Dowex 50W–X2 cation-exchange column. A yellow-green band was absorbed and later eluted with H_2SO_4 (0.5 M). This elution removed a well-defined yellow-green band, and its elution behavior conforms to an ionic charge of 2+. A fraction of higher charge with a similar color remained on the column. The spectrum of the eluted ion was identical with the spectrum in Figure 2. The molybdenum oxidation number and Cl/Mo ratio[8,9] were determined and are summarized in Tables II and III, respectively. The yellow-green eluate was passed through a JR, and the red reduction product was identified as $[Mo_2]^{4+}(aq)$.

A solution with a spectrum identical with I was produced by a 2-equiv oxidation of $[Mo_2]^{4+}(aq)$ in HCl (1 M) by H_2O_2. I is an air-sensitive ion and decays after a few hours even at 0 °C under nitrogen. The decomposition products have not been identified.

Disproportionation of $Mo_2(SO_4)_4^{3-}$ in Concentrated HCl. A sample of $K_3Mo_2(SO_4)_4 \cdot 3^1/_2H_2O$ was dissolved in concentrated HCl (12 N). A deep red-purple solution was formed instantaneously. A pink solid was produced upon addition of CsCl. The solid was filtered, analyzed, and found to be $Cs_3Mo_2Cl_9$. Anal. Calcd for $Cs_3Mo_2Cl_9$: Mo, 21.09; Cl, 35.09. Found: Mo, 20.92; Cl, 35.21. The ion in the deep red-violet filtrate was identified as $Mo_2Cl_8^{4-}$. $Mo_2Cl_9^{3-}$ is also generated by bubbling gaseous HCl through solution of the yellow-green ion, I.

$Mo_2(HPO_4)_4^{2-}$ in Aqueous Solution. The spectrum of II in H_3PO_4 has been recorded between 350 and 650 nm and given in Figure 3. The solution was prepared by dissolving $(pyH)_3[Mo_2(HPO_4)_4Cl]$ in aqueous H_3PO_4 (2 M) under nitrogen. The ion is light purple with absorption bands at 548 (ϵ = 107) and 428 nm (ϵ = 63). $Mo_2(HPO_4)_4^{2-}$ is stable in H_3PO_4 (2 M) if kept under nitrogen and does not show any decay after many hours at room temperature.

To a solution of $Mo_2(HPO_4)_4^{2-}$ in H_3PO_4 (2 M) was added zinc amalgam, and the solution was stirred vigorously under nitrogen. The light purple color was changed first to the pale blue-gray color of the phosphato complex of $[Mo_2]^{5+}$ in H_3PO_4[3] and then to the deep red color of the $[Mo_2]^{4+}$ complex.

Transformation of II to I. $(pyH)_3[Mo_2(HPO_4)_4Cl]$ was dissolved in HCl (2 M) under nitrogen at ca. 20 °C. The solution turned from light purple to yellow-green after ca. 20 min. The spectral change was recorded and shown in Figure 3. $Mo_2Cl_9^{3-}$ was produced by dissolving salts of $Mo_2(HPO_4)_4^{2-}$ in concentrated HCl.

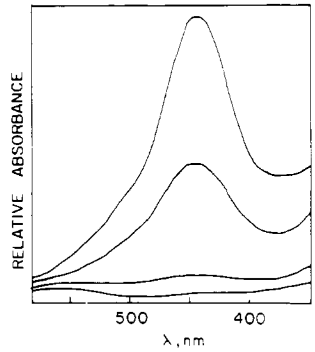

Figure 4. Spectral change in reaction 3.

Discussion

The results presented in this work prove the existence of species containing the unit $[\mathrm{Mo}\overset{3}{\text{—}}\mathrm{Mo}]^{6+}$ in aqueous solutions. The spectrum of an aqueous solution of an $Mo_2(HPO_4)_4^{2-}$ salt (Figure 3) is almost identical with the spectrum of this species in the solid state.[5] This fact proves that the structure of the aquated species is identical with the structure found in the crystal of $(py)_3[Mo_2(HPO_4)_4Cl]$ by X-ray technique,[5] i.e., $Mo_2(HPO_4)_4^{2-}$.

The interesting reversible disproportionation reaction of $Mo_2(SO_4)_4^{3-}$ in dilute HCl, described by Pernick and Ardon,[2] can be formulated as eq 1a (omitting the SO_4^{2-} and Cl^- ligands). I is the oxidation product of the disproportionation.

$$2[\mathrm{Mo}\overset{3.5}{\text{—}}\mathrm{Mo}]^{5+} \underset{+\mathrm{SO_4}^{2-}}{\overset{\mathrm{HCl}}{\rightleftarrows}} [\mathrm{Mo}\overset{4}{\text{—}}\mathrm{Mo}]^{4+} + \mathrm{I} \qquad (1a)$$

The above results suggest that I is, in fact, derived from the unit $[\mathrm{Mo}\overset{3}{\text{—}}\mathrm{Mo}]^{6+}$ and is a mixture of chloro complexes of this unit having the general composition $[Mo_2Cl_n(H_2O)_{8-n}]^{(6-n)+}$. The ion-exchange chromatography showed that this mixture can be separated. One fraction was found to be a 2+ cation with a Cl/Mo ratio of 2 to which the structure $[Cl_2(H_2O)_2Mo{\equiv}Mo(H_2O)_2Cl_2]^{2+}$ was assigned. The spectrum of this ion, having a maximum at 430 nm is very similar to those of the other species included in I, $[Mo_2Cl_n(H_2O)_{8-n}]^{(6-n)+}$, since this band is probably due to the $[\mathrm{Mo}\overset{3}{\text{—}}\mathrm{Mo}]^{6+}$ unit. A similar constancy of spectrum is known in the case of Mo_2^{4+}.[1] $Mo_2Cl_8^{4-}$ and all of its aquation products, including $[Mo_2]^{4+}(aq)$, have a maximum at about 510 nm which belongs to the $[\mathrm{Mo}\overset{4}{\text{—}}\mathrm{Mo}]^{4+}$ unit.

The two-electron oxidation of the unit $[\mathrm{Mo}\overset{4}{\text{—}}\mathrm{Mo}]^{4+}$ in HCl is formulated as eq 2. Finally, the substitution of HPO_4^{2-} ligands in II by Cl^- in aqueous HCl produce the same product I (eq 3).

$$[Mo_2Cl_n(H_2O)_{8-n}]^{(4-n)+} \rightarrow [Mo_2Cl_n(H_2O)_{8-n}]^{(6-n)+} + 2e^- \qquad (2)$$

$$Mo_2(HPO_4)_4^{2-} + nCl^- \rightarrow [Mo_2Cl_n(H_2O)_{8-n}]^{(6-n)+} + 4HPO_4^{2-} \qquad (3)$$

Reaction 1a can be reformulated (omitting the SO_4^{2-} and Cl^- ligands) as

$$2[\mathrm{Mo}\overset{3.5}{\text{—}}\mathrm{Mo}]^{5+} \underset{+\mathrm{SO_4}^{2-}}{\overset{\mathrm{HCl}}{\rightleftarrows}} [\mathrm{Mo}\overset{4}{\text{—}}\mathrm{Mo}]^{4+} + [\mathrm{Mo}\overset{3}{\text{—}}\mathrm{Mo}]^{6+} \qquad (1b)$$

In contrast to the relatively labile and easily oxidizable species I and II the ion $Mo_2Cl_9^{3-}$ with its three bridging μ-Cl^-

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(10) Qualitative analysis of Mo_2^{4+}: A typical deep blue color of $Mo_2(NCS)_8^{4-}$ which appears immediately upon addition of KNCS to complexes of Mo_2^{4+}[12] was used to detect this species in reaction mixtures.

(11) Kolthoff, I. M., Sandell, E. "Textbook of Quantitative Inorganic Analysis", 3rd ed.; Macmillan: New York, 1959; p 545.

(12) Bino, A.; Cotton, F. A.; Fanwick, P. F. *Inorg. Chem.* **1979**, *18*, 3558.

ligands is extremely inert and once formed in concentrated HCl does not decompose in more dilute acids to yield the former species.

Preliminary results show that $Mo_2(HPO_4)_4^{2-}$ undergoes substitution in aqueous H_2SO_4. Single crystals of a $Mo_2(SO_4)_4^{2-}$ salt have not been obtained yet.

Registry No. I (n = 4), 75365-58-1; II, 75365-59-2; $[Mo_2]^{4+}$, 11083-49-1; $Cs_3Mo_2Cl_9$, 29013-02-3; $K_3Mo_2(SO_4)_4$, 63311-41-1; $(pyH)_3[Mo_2(HPO_4)_4Cl]$, 71597-13-2.

Contribution from the Chemical Technology Division,
Australian Atomic Energy Commission, Sydney, Australia

Gas-Phase Properties of Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)(trimethyl phosphato)dioxouranium(VI)

A. Ekstrom* and C. H. Randall

Received May 12, 1980

Compounds of the type $UO_2(HFA)_2X$, where HFA represents the 1,1,1,5,5,5-hexafluoropentane-2,4-dionato ion and X represents a neutral ligand such as trimethyl phosphate (TMP) or triphenylphosphine oxide (TPPO), have been known for some years[1,2] and, because of their volatility, have been recommended for the gas chromatographic determination of uranium.[3] The crystal structures of the two isomorphs[4,5] and some thermochemical properties[6] of $UO_2(HFA)_2TMP$ have been reported, while more recent studies have described the preparation,[7] crystal structure,[8] and gas-phase properties and dimerization equilibria[9] of anhydrous $UO_2(HFA)_2$.

The demonstration of the existence of $UO_2(HFA)_2$ in the gas phase suggests that compounds such as $UO_2(HFA)_2TMP$ might exist in the gas phase as partly or wholly dissociated molecules (eq 1), and the present work was undertaken to

$$UO_2(HFA)_2TMP \rightleftharpoons UO_2(HFA)_2 + TMP \qquad (1)$$

explore the possibility of this reaction. It might be noted that recent work by Kaldor et al.[10,11] has shown that laser irradiation under molecular beam conditions of the compound $UO_2(HFA)_2THF$ (THF = tetrahydrofuran) at a laser frequency corresponding to the ν_3 absorption of the uranyl group leads to the dissociation of the molecule to form free THF and, presumably, monomeric $UO_2(HFA)_2$.

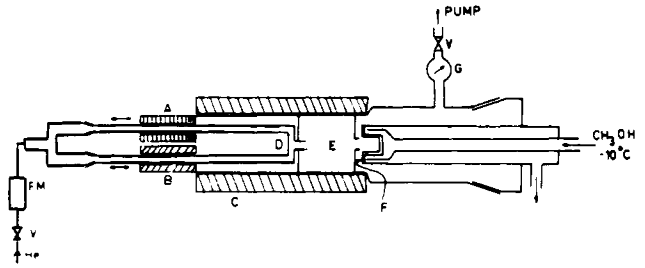

Figure 1. Apparatus to measure the gas-phase neutral ligand exchange: U, needle valve; FM, flow meter, calibrated for helium; A and B, tube furnaces movable horizontally; C, fixed tube furnace; D, mixing chamber; E, reaction chamber; F, cold finger insert; G, pressure gauge.

Table I. Summary of Vapor Pressure Measurements (log [P (Pa)] = A − 1000B/K)

compd	temp range, K	A	B	ΔH, kJ mol^{-1}
$UO_2(HFA)_2TMP$	365-414 (melt)	11.6 ± 0.1	4.0 ± 0.1	76 ± 2
$UO_2(HFA)_2TPPO$	406-442 (melt)	12.1 ± 0.5	5.2 ± 0.2	99 ± 4

Table II. Results of Test of Separation Procedure

input material, mg		duration of sublimation of $UO_2(HFA)_2$-TMP, h	recovered material			
			TMP		TPPO	
TMP (0.713% ^{235}U)	TPPO (0.408% ^{235}U)		wt, mg	% ^{235}U	wt, mg	% ^{235}U
36.4	46.3	2	34.8	0.709	45.2	0.410
52.3	30.4	4	51.0	0.714	28.7	0.409

Experimental Section

$UO_2(HFA)_2TMP$ and $UO_2(HFA)_2TPPO$ containing uranium of both natural (0.713% uranium-235) and depleted (0.408% uranium-235) isotopic content were prepared as described previously,[6] the diethyl ether being replaced by the stoichiometric quantity of the neutral ligand in the preparation. All compounds were purified by at least four successive sublimations.

The gas-phase neutral-ligand-exchange experiments were carried out with the apparatus shown in Figure 1, the gas-phase concentrations of the TMP and TPPO complexes being controlled by the temperatures of furnaces A and B. The temperature of furnace C was controlled at 250 °C, and the helium carrier-gas pressure was 2.7 kPa for all runs. The residence time was controlled by the carrier-gas flow rate and by the volume of the reaction chamber.

In a typical experiment, samples of the two compounds were placed in glass boats at positions A and B, the carrier-gas pressure was established at the desired flow rate, and furnace C was heated to 250 °C. Furnaces A and B were then heated to the required temperature and moved into position. The compounds were volatilized, mixed in the mixing chamber D, allowed to flow through the reaction chamber E, and condensed as a solid on the cold finger insert F. At the end of the run, the cold finger insert together with the deposited compounds was removed and weighed, the TMP complex selectively sublimed off at 80 °C, the cold finger insert reweighed, the TPPO complex sublimed off at 150 °C, and the empty cold finger insert reweighed. From the above, the total quantities of the TMP and TPPO complexes which passed through the reaction chamber in a given time could be obtained, and the average gas-phase concentrations of the TMP and TPPO complex could be calculated. Samples of the sublimed TMP and TPPO complexes were then converted to $UO_2(NO_3)_2$ and analyzed for their uranium-235 content with a Metropolitan-Vickers MS5 mass spectrometer.

The vapor pressure measurements and the determination of the equilibrium constant for reaction 1 were carried out with the apparatus and experimental procedures described in detail elsewhere.[9]

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(1) W. C. Butts and C. V. Bank, *Anal. Chem.*, **42**, 133 (1970).
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